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(54) [Name of the invention]

Polyolefin Type Fiber With Excellent Hydrophilic Properties and Its Manufacturing Method

(57) [Summary]

[Topic]

A polyolefin type fiber with excellent hydrophilic properties is obtained without sacrificing the inherent to the polyolefin mechanical strength, chemical resistant properties etc.

[Solution measures]

On the surface of, (1) a polypropylene fiber that is formed from syndiotactic polypropylene, (2) a blended fiber that is formed from an olefin type polymer containing at least 30 weight % of syndiotactic polypropylene, or (3) a wick-shell type composite fiber, that has a structure obtained as the wick part is made from olefin type polymer and the shell part is made from syndiotactic polypropylene or an olefin type polymer that contains at least 30 weight % or more of syndiotactic polypropylene, an oxidation treatment is conducted by using the electron beam (e-beam) radiation method, the gamma ray radiation method, the ultra-violet beam radiation method, the photon method, the flame method, the corona electrical discharge method, the glow electrical discharge method, and by that oxygen containing functional radicals are incorporated and hydrophilic properties are imparted.

[Range of the claims of the invention]


[Claim 1]

Polyolefin type fiber, characterized by the fact that it is a fiber that is any one type selected from the described here below (1) ~ (3) fibers, and where by an oxidation treatment, on the surface of the above described fiber oxygen containing functional radicals are incorporated and by that hydrophilic properties are imparted.

- (1) Polypropylene fiber formed from syndiotactic polypropylene.
- (2) Blended fiber, that is formed from an olefin type polymer that contains at least 30 weight % or more of syndiotactic polypropylene.
- (3) A wick- shell type composite fiber, that has a structure obtained as the wick part is made from olefin type polymer and the shell part is made from syndiotactic polypropylene or an olefin type polymer that contains at least 30 weight % or more of syndiotactic polypropylene.


[Claim 2]

Manufacturing method for the preparation of polyolefin type fiber, characterized by the fact that it is a manufacturing method for the preparation of the reported according to the Claim 1 of the present invention, reported here above, and it is a method where an oxidation treatment is conducted by using at least one of the electron beam radiation method, the gamma ray radiation method, the ultra-violet beam radiation method, the photon method, the flame method, the corona electrical discharge method, the glow electrical discharge method, and by that oxygen containing functional radicals are incorporated on the surface of the fibers.



[Claim 3]

Manufacturing method for the preparation of the polyolefin type fiber according to the described here above Claim 2 of the present invention, characterized by the fact that for the incorporation of oxygen containing functional radicals on the surface of the fiber, by using an oxidation treatment, at least one type of gas is used that is selected from the group of air, oxygen, CO, CO₂, He, Ar, sulfur oxides, and nitrogen oxides.



[Claim 4]

Manufacturing method for the preparation of the polyolefin type fiber according to the described here above Claim 2 or Claim 3 of the present invention, characterized by the fact that it is a method where at least one type of compound selected from the group of acrylic acid, methacrylic acid, methacryl sulfonic acid, and styrene sulfonic acid, is coated on the surface of the fiber and after that on the above described fiber surface, by using an oxidation treatment oxygen containing functional radicals are introduced.

[Claim 5]

Manufacturing method for the preparation of polyolefin type fiber, characterized by the fact that it is a manufacturing method for the preparation of the polyolefin fiber reported according to Claim 1 of the present invention, and by using an oxidation treatment, oxygen containing functional radicals are introduced at the surface of the fiber, and the fiber surface is contained with at least one acid selected from the group of fuming sulfuric acid, concentrated sulfuric acid, and chlorosulfonic acid.

[Detailed explanation of the invention]

[0001]

[Technological sphere pertinent to the present invention]

The present invention is an invention about a polyolefin type fiber, and in more details, the present invention is an invention about a polyolefin type fiber where excellent hydrophilic type properties are imparted without decreasing the mechanical strength of the fiber.

[0002]

[Previous technology]

Usually, the polyethylene, polypropylene etc., polyolefins, have excellent mechanical properties and they are inexpensive, and they are excellent from the point of view of fiber processing properties and cost, and then also, their chemical resistance properties and especially the high temperature alkali resistance properties are extremely excellent. In recent years, these characteristics have come to life, and the development in the sphere of the polyolefin type fiber industrial resources and especially, the developments in the area of the nonwoven fabric materials, have been significant. However, in the case of the polyolefin type materials, the adhesive properties and the hydrophilic properties are very poor, and because of that, at the present time the situation is such that the area of application of the polyolefin type fiber is limited, and it is desirable that the application field is widened by improving these drawbacks.

[0003]

For example, in the case of the asbestos substituting fibers, that are used for cement reinforcement, strength, alkali resistance properties under high temperature, cement compatibility properties, water dispersibility properties etc., are required. However, the polypropylene has very poor compatibility properties relative to the cement material, etc., and because of that, an improvement is desired. Also, for the material used as a separator for alkali electrical batteries, alkali resistance properties, hydrophilic properties, oxidation resistance properties, etc., are required. Then, also in filtration fabrics, wet type filters, etc., the same way, because of the chemical resistance properties, the mechanical strength, in many cases polyolefins, and especially, polypropylene is widely used,

however, an improvement of the hydrophilic properties is required. However, in the case of a material where sulfuric acid radicals are incorporated by a hydrophilization treatment using sulfuric acid etc., because of the treatment, there is a deterioration of the polyolefin fiber and together with that the mechanical strength is deteriorated. Also, by using the hydrophilization treatment using a gas phase, like the plasma treatment, the electron beam radiation treatment, etc., the same way, there is a deterioration of the polyolefin type fiber material. Because of that the invention of a polyolefin type fiber with an excellent balance of the mechanical properties and hydrophilic properties, is desired. Namely, if the hydrophilization treatment is conducted according to the above described methods, a deterioration of the fiber occurs, and the inherent to the polyolefin type fiber mechanical properties are not demonstrated and because of that there is the drawback point that the hydrophilization level is decreased or excellent mechanical strength is not obtained. And then, if the hydrophilization level is increased excessively, there is the drawback that the chemical resistance properties are also decreased.

[0004]

[Problems solved by the present invention]

Regarding the present invention, it is an invention that solves problem points according to the previous technology as those described here above, and it is an invention that is suggesting a polyolefin type fiber with excellent hydrophilic properties, without sacrificing the inherent to the polyolefin mechanical strength, chemical resistant properties etc.

[0005]

[Measures in order to solve the problems]

The authors of the present invention have conducted rigorous research regarding the above described problems and as a result from that they have observed that by using, at least on the fiber surface, a syndiotactic polypropylene material, the above described problems have been solved. And by that the present invention has been completed. And namely, the present invention is an invention about a polyolefin type fiber, characterized by the fact that on the surface of, (1) a polypropylene fiber that is formed from syndiotactic polypropylene, (2) a blended fiber that is formed from an olefin type polymer containing at least 30 weight % of syndiotactic polypropylene, or (3) a wick-shell type composite fiber, that has a structure obtained as the wick part is made from olefin type polymer and the shell part is made from syndiotactic polypropylene or an olefin type polymer that contains at least 30 weight % or more of syndiotactic polypropylene, an oxidation treatment is conducted, and by that oxygen containing functional radicals are incorporated and hydrophilic properties are imparted.

[0006]

[Practical implementation conditions of the present invention]

Regarding the used according to the present invention definition of syndiotactic polypropylene, it has the meaning that the ratio of the pendant fraction is at least 0.5 or above. Regarding the used here notion of pendant ratio, it represents the ratio between the intensity of the peak at approximately 20 ppm (corresponding to the syndiotactic pendant) and the peak intensity based on the methyl radicals of all the propylene monomer units, as measured according to the ^{13}C -NMR measurement. In the past, at the time of the manufacturing of the syndiotactic polypropylene, as a catalyst material, vanadium compound has been used, however, by using that, it has not been possible to obtain a material that has a pendant ratio of at least 0.5 or higher, and not only that, but also, it is a material that has not been manufactured industrially, on a large scale. However, in recent years, it has been possible to obtain polypropylene with a high syndiotacticity, where the pendant ratio exceeded 0.7, by using a catalyst material, that is formed from a transition metal compound that has an asymmetric configurational electron and aluminoxane. As the syndiotactic polypropylene that is used according to the present invention, it is preferred to be a material that has a pendant ratio of at least 0.6 or more, and more preferably, it is a material with a pendant ratio of at least 0.7 or more. Also, regarding this syndiotactic polypropylene, it is a good option if it is propylene homopolymer material, or a copolymer material that is formed from propylene and ethylene and/or α -olefin, and it is practically a syndiotactic polypropylene material.

[0007]

As the manufacturing method for the preparation of the syndiotactic polypropylene material according to the above described, for example, there is the manufacturing method that has been described according to the description of the Japanese Patent Application Laid Open Number Hei-Sei 3-179006. As the polymerization catalyst material, it is possible to use both an asymmetric configuration electron possessing crosslinking type transition metal compound and a catalyst aid. However, it is also possible to use catalysts with different structures that that, provided that they are materials that allow the manufacturing of polypropylene with a pendant ratio of at least 0.6 or higher. And also there are no limitations regarding the polymerization methods of the polypropylene material, and it is possible to appropriately use the solvent polymerization method utilizing an inert solvent material, or the agglomeration polymerization method, or the gas phase polymerization method.

[0008]

After that, regarding the meaning of the olefin type polymer according to the present invention, it represents polyethylene, polypropylene, polybutyl pentene, etc., and also it is a good option if it is a copolymer material, like an ethylene - propylene copolymer, and these can be random copolymers or graft copolymers, block copolymers etc. According to the present invention, these olefin type polymers can be used individually and it is a good option, and they can also be used as a blend.

[0009]

Regarding the blended type fiber obtained from syndiotactic polypropylene and an olefin type polymer, it is preferred that a material is used where syndiotactic polypropylene is at least 30 weight %, and preferably it is at least 40 weight % or more. Regarding the reason for that, it is due to the fact that in the case when it is less than 30 weight %, at the time of the imparting of the hydrophilic properties, the effect of the syndiotactic polypropylene that it is difficult to deteriorate the macromolecular chain, is not observed.

[0010]

There are no particular limitations regarding the fiber spinning conditions for the manufacturing of the polyolefin type fiber according to the present invention, and it can be manufactured according to the usual manufacturing methods. Namely, in the case of the syndiotactic polypropylene fiber (1), the fiber spinning temperature used is in the range of 230 ~ 300°C, and also, in the case of the wick - shell type composite fiber, because in the shell part syndiotactic polypropylene is used, the fiber spinning temperature is in the range of 230 ~ 300°C, and because in the wick part a polyolefin type polymer is used, usually, it is in the range of 200 ~ 300°C. The same way, in the case of the blended type fiber (2), depending on the blending ratio, it is usually set in the range of 200 ~ 300°C. There are also no particular limitations regarding the blending methods, and it is also a good option if in advance, in the extruder equipment the materials are blended, and the obtained pellets are spun into fiber material, and also, it is a good option if a method is used where the predetermined amounts of the different types of pellets or powder form materials, are supplied by using a gravity feeder, and then the fiber material is spun. Also, according to the present invention, in order to increase the mechanical strength, it is desirable that the fiber spun fiber material is elongated at an elongation ratio of at least 3 times or more, and a heated water elongation is preferred.

[0011]

Moreover, in the fiber material according to the present invention, there is no problem, if depending on the requirements, an anti-oxidation agent, an ultra-violet light absorption agent, etc., stabilizing agents, an anti-electrostatic agent, a flame retardant agent, and a dye material, pigmenting material etc., coloring materials are used.

[0012]

After that, as the oxidation treatment according to the present invention, it is a treatment where on the fiber surface, practically, oxygen containing functional radicals (-COOH, -OH, -C=O, -SO₃, -NO₃ radicals etc.), are incorporated. By the incorporation of these functional radicals at the surface of the fiber material, it is possible to impart hydrophilic properties to such olefin type fibers as the described here above.

[0013]

According to the present invention, as the oxidation treatment used to incorporate oxygen containing radicals at the surface of the fiber material, there are the electron beam (e-beam) radiation method, the gamma ray radiation method, the ultra-violet beam radiation method, the photon method, the flame method, the corona electrical discharge method, the glow electrical discharge method. These oxidation treatment methods can be used individually or they can be used together as a combination of 2 or more methods.

Regarding these methods, they can be also conducted under normal temperature and normal pressure, and it is a good option, and it is a good option if they are conducted in an environment where as the inert gas, it is possible to use He, Ar, and as a reactive gas, it is possible to use air, oxygen, nitrogen, CO, CO₂, sulfur oxides (for example, SO₂, SO₃, etc.), or nitrogen oxides (for example, NO, NO₂, N₂O etc.). Regarding this inert gas and reactive gas, when the electrical field is applied, they generate different types of chemical species (electrons, ions, radicals, excited molecules etc.). And as a result from that, it becomes easy for a reaction with the polymers forming the structure of the fiber material, to occur, and this brings about the result of incorporating oxygen containing functional radicals at the surface of the fiber material.

[0014]

Also, it is possible to have the method where for the incorporation of the oxygen containing radicals at the surface of the fiber material, a monomer that demonstrates hydrophilic properties, is coated in advance on the surface of the fiber material, and after that by using an oxidation treatment, oxygen containing radicals are incorporated on the surface of the fiber material. In this case, as the compounds that can be coated on the surface of the fiber material, there are the following here below materials: acrylic acid, methacrylic acid, methacryl sulfonic acid, acryl sulfonic acid, styrene sulfonic acid etc., hydrophilic properties presenting monomers. Regarding these compounds, after the coating, by using the electron beam radiation method, the gamma ray radiation method, the plasma treatment method etc., methods of the above described oxidation treatment, these are fixed on the surface of the fiber. And these compounds can be used individually, and it is a good option, and they can be used together as a combination of two or more, and it is also a good option.

[0015]

Regarding the used according to the present invention fiber surface oxidation treatment method where an acid and a catalyst material, are used, as the acid, an acid is used that is selected from the group of fuming sulfuric acid, concentrated sulfuric acid, and chlorosulfonic acid. And these compounds can be used individually, and it is a good option, and they can be used together as a combination of two or more, and it is also a good option. There are no particular limitations regarding the method of contacting the fiber surface and the acid, however, the method where the above described polyolefin type fibers are directly immersed in the acid, can be appropriately used. For example, in

the case when concentrated sulfuric acid is used, it is usually an immersion, that is conducted at a temperature in the range of 50 ~ 120°C and for a period of time in the range of 5 ~ 60 minutes.

[0016]

[Effect]

According to the present invention, a syndiotactic polypropylene is used and because of that, there is deterioration of the polyolefin type fibers occurring, and it is possible to conduct a hydrophilization treatment on its surface. As a result from that, there is no loss of the mechanical properties and chemical resistance properties inherent to the polyolefin type fiber material. And in the case of this invention it is possible to suggest a polyolefin type fiber that has an excellent balance of the hydrophilic properties, the mechanical properties and the chemical resistance properties.

[0017]

[Practical Examples]

Here below, the present invention will be explained in more details by using practical implementation examples. Moreover, the present invention is by no means limited by the below described practical implementation examples.

[0018]

(Resin properties)

In table 1, the properties of the resins used according to the described here below Practical Examples and reference Examples, are presented.

[0019]

[Table 1]

	MFR (*) (g/10 min)	Other than that
polypropylene (1)	30	-
syndiotactic polypropylene	25	pendant ratio 0.78
polyethylene (1)	23	-

(*) MFR: melt flow value (measured according to the described here below method).

(1) case of polypropylene: JIS K6758

(2) case of polyethylene: JIS K 6760

[0020]

(Polymerization of the syndiotactic polypropylene)

Regarding the shown according to Table 1 syndiotactic polypropylene, it is a material that is polymerized according to the described here below. First, as it has been reported in the J. Am. Chem. Soc. 1987, Number 109, page 6544, isopropyl cyclopentadienyl - 1-fluorene is transformed into a lithium salt, and it is reacted with a zirconium tetrachloride, and by that, isopropyl (cyclopentadienyl - 1-fluorenyl) zirconium dichloride is synthesized. After that, 0.33 moles of triethyl aluminum are dissolved in 2 ml toluene, and this is added into a reaction vessel, and the temperature of the reaction vessel is set at 70°C. Then, 1500 ml of propylene are added into the reaction vessel, and this is then stirred for a period of 10 minutes. 45 mg of tris (pentafluorophenyl) boron is dissolved in 20 ml toluene, and the same way, 35 mg of isopropyl (cyclopentadienyl - 1-fluorenyl) zirconium chloride, is dissolved in 25 ml toluene and after that the two types of toluene solutions are mixed together for a period of 5 minutes. This mixed catalyst material is added into a 50 ml stainless steel bomb, and after that, 200 ml propylene are added into the reaction vessel as they pass through the above bomb. The content in the reaction vessel is stirred and reacted for approximately 30 minutes. The unreacted propylene is taken out of the reaction vessel, and the reaction synthesized material is washed by using acetone, and it is then dried under vacuum.

[0021]

(Measurement of the tacticity of the syndiotactic polypropylene)

The ratio between the intensity at approximately 20 ppm (rrrr), that is observed in the ¹³C - NMR measurement, and the peak intensity associated with the methyl radicals of all the propylene monomer units (mm, mr, rr), is measured. Then according to the described here below formula, the syndiotactic pendant ratio is calculated.

[0022]

Syndiotactic Pendant ratio (%) = $\frac{rrrr}{(mm + mr + rr)} \times 100$

[0023]

(Practical Example 1)

Under the conditions shown according to the presented here below Table 2, the syndiotactic polypropylene was melted and fiber spun and after that, it was thermally oriented, and a filament with a fineness of 3 d (denier, this has the same meaning here below), and a staple with a fiber length of 51 mm, was obtained. After that, by using this

staple, and by using a roller carding equipment, a web was manufactured, and by using a Spanres equipment a nonwoven fabric material with a weight per surface area of 40 g/m², was obtained. After that, this nonwoven fabric material and the above described filament were placed in a reaction vessel, and under a normal temperature and normal pressure, and by using 200 KV applied electrical field, a corona electrical discharge treatment was conducted, and by that the hydrophilization treatment of the fiber surface, was conducted.

[0024]

(Practical Example 2)

Under the conditions shown according to the presented here below Table 2, 60 weight % of polypropylene (1) and 40 weight % of syndiotactic polypropylene were blended and then this material was melted and fiber spun and after that, it was thermally oriented, and a filament with a fineness of 3 d (denier, this has the same meaning here below), and a staple with a fiber length of 51 mm, was obtained. After that, by using the same technological procedures as described according to the Practical Example 1, a nonwoven fabric material with a weight per surface area of 40 g/m², was obtained. After that, this nonwoven fabric material and the above described filament were subjected to a corona electrical discharge treatment, that was conducted by using the same technological procedures as described according to the Practical Example 1, and by that the hydrophilization treatment of the fiber surface, was conducted.

[0025]

(Practical Example 3)

Under the conditions shown according to the presented here below Table 2, 30 weight % of polyethylene (1) and 70 weight % of syndiotactic polypropylene were blended and then this material was melted and fiber spun and after that, it was thermally oriented, and a filament with a fineness of 3 d (denier, this has the same meaning here below), and a staple with a fiber length of 51 mm, was obtained. After that, by using the same technological procedures as described according to the Practical Example 1, a nonwoven fabric material with a weight per surface area of 40 g/m², was obtained. After that, this nonwoven fabric material and the above described filament were subjected to a corona electrical discharge treatment, that was conducted by using the same technological procedures as described according to the Practical Example 1, and by that the hydrophilization treatment of the fiber surface, was conducted.

[0026]

(Practical Example 4)

The same filament and nonwoven fabric material, as those obtained by using the same technological procedures as described according to the Practical Example 2, were

immersed in acrylic acid and after that they were placed in a reaction vessel, and under a nitrogen ambient atmosphere, an electron beam of 4 Mrad was irradiated, and by that the hydrophilization treatment of the fiber surface, was conducted.

[0027]

(Practical Example 5)

The same filament and nonwoven fabric material, as those obtained by using the same technological procedures as described according to the Practical Example 2, were immersed in acrylic acid and after that they were placed in a reaction vessel, and they were irradiated using ultra-violet beam, at a wavelength of at least 200 nm or higher, and by that the hydrophilization treatment of the fiber surface, was conducted.

[0028]

(Practical Example 6)

The same filament and nonwoven fabric material, as those obtained by using the same technological procedures as described according to the Practical Example 2, were placed in a reaction vessel, and under an ambient atmosphere containing 70 % He and 30 % air, and under a normal temperature and normal pressure, a high frequency electrical voltage of 5 KHz was applied and a glow electrical discharge was conducted , and by that the hydrophilization treatment of the fiber surface, was conducted.

[0029]

(Practical Example 7)

The same filament and nonwoven fabric material, as those obtained by using the same technological procedures as described according to the Practical Example 1, were immersed heated to 80oC, 98 % concentrated sulfuric acid for a period of 20 minutes, and after that this was neutralized and washed and dried, and by that the hydrophilization treatment of the fiber surface, was conducted.

[0030]

[Table 2]

Table 2: Fiber spinning conditions

	Weight ratio (%)	Fiber spinning temperature (oC)	Elongation ratio (times)	Elongation temperature (oC)
Practical Example 1	100(s-PP only)	260	3.5	80

Practical Example 2	blend (s-PP/PPI=40/60)	250	3.5	70
Practical Example 3	blend (s-PP/PEI=70/30)	250	3.5	70
Practical Example 4	blend (s-PP/PPI=40/60)	250	3.5	70
Practical Example 5	blend (s-PP/PPI=40/60)	250	3.5	70
Practical Example 6	blend (s-PP/PPI=40/60)	250	3.5	70
Practical Example 7	blend 100 (s-PP only)	260	3.5	80

PP1: polypropylene (1)

s-PP: syndiotactic polypropylene

PE: polyethylene (1)

[0031]

(Practical Example 8)

Under the conditions shown according to the presented here below Table 3, a wick - shell type composite fiber, that uses in its wick part polypropylene (1) and in its shell part syndiotactic polypropylene, was spun and after that, it was thermally oriented, and a filament with a fineness of 3 d (denier, this has the same meaning here below), and a staple with a fiber length of 51 mm, was obtained. After that, by using a roller carding equipment, a web was manufactured, and by using a Spanres equipment a nonwoven fabric material with a weight per surface area of 40 g/m², was obtained. After that, this nonwoven fabric material and the above described filament were placed into a reaction vessel and under normal temperature and normal pressure, and by using an applied field of 200 KV, a corona electrical discharge treatment was conducted, and by that the hydrophilization treatment of the fiber surface, was conducted.

[0032]

(Practical Example 9)

Under the conditions shown according to the presented here below Table 3, a wick - shell type composite fiber, that uses in its wick part polypropylene (1) and in its shell part a blended polymer obtained from syndiotactic polypropylene and polypropylene (1), was fiber spun and after that, it was thermally oriented, and a filament with a fineness of 3 d, and a staple with a fiber length of 51 mm, was obtained. After that, by using a roller carding equipment, a web was manufactured, and by using a Spanres equipment a nonwoven fabric material with a weight per surface area of 40 g/m², was obtained. After

that, this nonwoven fabric material and the above described filament were placed into a reaction vessel and under normal temperature and normal pressure, and by using an applied field of 200 KV, a corona electrical discharge treatment was conducted, and by that the hydrophilization treatment of the fiber surface, was conducted.

[0033]

(Practical Example 10)

The same filament and nonwoven fabric material, as those obtained by using the same technological procedures as described according to the Practical Example 8, were immersed in styrene sulfonic acid and after that they were placed in a reaction vessel, and under a nitrogen ambient atmosphere, an electron beam of 4 Mrad was irradiated, and by that the hydrophilization treatment of the fiber surface, was conducted.

[0034]

(Practical Example 11)

The same filament and nonwoven fabric material, as those obtained by using the same technological procedures as described according to the Practical Example 8, were placed in a reaction vessel, and in an ambient atmosphere containing 90 %Ar and 10 % of a mixed gas containing nitrogen, water, oxygen, CO₂, and under a normal temperature and normal pressure, a high frequency electrical voltage of 5 KHz was applied and a glow electrical discharge was conducted, and by that the hydrophilization treatment of the fiber surface, was conducted.

[0035]

[Table 3]

Table 3: Fiber spinning conditions

	Weight ratio (%)		Fiber spinning temperature (oC)		Elongation ratio (times)	Elongation temperature (oC)
	wick	shell	wick	shell		
Practical Example 8 70	PP1 =70	s-PP=30	250		260	3.5
Practical Example 9 70	PP1=60	s-PP/PP1=20/20	250		260	3.5

Practical Example 10 PP1 =70 s-PP=30 70	250	260	3.5
Practical Example 11 PP1 =70 s-PP=30 70	250	260	3.5

PP1: polypropylene (1)

s-PP: syndiotactic polypropylene

[0036]

(Reference Example 1)

Under the conditions shown according to the presented here below Table 4, polypropylene only was used and this was melted and fiber spun and after that, it was thermally oriented, and a filament with a fineness of 3 d, and a staple with a fiber length of 51 mm, was obtained. After that, by using this staple fiber, according to the same technological procedures as those used in the case of the Practical Example 1, a nonwoven fabric material with a weight per surface area of 40 g/m², was obtained.

[0037]

(Reference Example 2)

The strength of the syndiotactic polypropylene obtained according to the Practical Example 1, and the water absorption of the obtained nonwoven fabric material, were measured.

[0038]

(Reference Example 3)

The same filament and nonwoven fabric material as those obtained according to the technological procedures of the Reference Example 1 was subjected to a corona electrical discharge treatment under the same conditions as in the case of the Practical Example 1, and a hydrophilization treatment was conducted on the surface of the fiber material.

[0039]

(Reference Example 4)

The same filament and nonwoven fabric material as those obtained according to the technological procedures of the Reference Example 1 was immersed in acrylic acid under the same conditions as in the case of the Practical Example 4, and after that this was placed in a reaction vessel and under a nitrogen ambient atmosphere an electron beam at

4 Mrad was irradiated and by that a hydrophilization treatment was conducted on the surface of the fiber material.

[0040]

(Reference Example 5)

Under the conditions shown according to the presented here below Table 4, 90 weight % of polypropylene (1) and 10 weight % of syndiotactic polypropylene were blended and then this material was melted and fiber spun and after that, it was thermally oriented, and a filament with a fineness of 3 d, and a staple with a fiber length of 51 mm, was obtained. After that, by using this staple fiber and the same technological procedures as described according to the Practical Example 1, a nonwoven fabric material with a weight per surface area of 40 g/m², was obtained. After that, this nonwoven fabric material and the above described filament were subjected to a corona electrical discharge treatment, that was conducted by using the same technological procedures as described according to the Practical Example 1, and by that the hydrophilization treatment of the fiber surface, was conducted.

[0041]

[Table 4]

Table 4: Fiber spinning conditions

	Weight ratio (%)	Fiber spinning temperature (oC)	Elongation ratio (times)	Elongation temperature (oC)
Reference Example 1	100(s-PP only)	250	3.5	70
Reference Example 2	100(s-PP only)	260	3.5	80
Reference Example 3	100(s-PP only)	250	3.5	70
Reference Example 4	100(s-PP only)	250	3.5	70
Reference Example 5	blend s-PP/PP1=10/90	250	3.5	70

PP1: polypropylene (1)

s-PP: syndiotactic polypropylene

[0042]

The results from the measurements of the strength of the filaments obtained according to the above described Practical Examples 1 ~ 11 and the Reference Examples 1 ~ 5, and the

water absorption of the obtained nonwoven fabric materials, are shown in the presented here below Table 5. Moreover, the methods for the property evaluation are according to the described here below.

[0043]

[Water absorption]

The obtained nonwoven fabric sheet is made into an experimental piece with a width of 25 mm and a length of 300 mm, and one edge of the sheet was immersed vertically in deionized water (immersion depth 20 mm), and after 10 minutes, the height of the absorbed liquid (in mm) was obtained, and this was used as the water absorption degree.

[0044]

[Fiber tensile strength]

The obtained filaments (prior to the hydrophilization treatment and after the treatment) were immersed in acrylic acid and they were then measured under the conditions specified according to the regulations of the JIS L 1013.

[0045]

Table 5]

Table 5: Properties Table

表 5 物性表 1 1 3 4

	強度 (g/d)		吸水度 (mm)
	処理前	処理後	
実施例 1	7.2	6.8	152
実施例 2	5.9	5.1	147
実施例 3	4.8	4.2	137
実施例 4	5.9	5.3	150
実施例 5	5.9	5.1	144
実施例 6	5.9	5.4	145
実施例 7	7.2	6.1	148
実施例 8	6.3	5.9	153
実施例 9	6.5	6.0	146
実施例 10	6.3	5.7	132
実施例 11	8.3	5.8	170
比較例 1	6.6	—	19
比較例 2	7.2	—	21
比較例 3	6.6	3.2	148
比較例 4	6.6	3.0	152
比較例 5	6.3	3.8	150

prior to the treatment: prior to the hydrophilization treatment
after the treatment: after the hydrophilization treatment

Headings in the table:

1. Practical Examples, 2. Reference Examples, 3. Strength (g/d), prior to the treatment// after the treatment, 4. Water absorption degree.

[0046]

From the Reference Examples 1 and 2, it is evaluated that in the case when either the usual polypropylene or syndiotactic polypropylene are used, if a hydrophilization treatment is not conducted, the water absorption degree is extremely poor. Also, as it is shown in the Practical Examples 1 ~ 11, it is understood that if any of the different types of hydrophilization methods are used, the water absorption is extremely increased, and also, it is evaluated that there is almost no change in the fiber strength prior to and after the hydrophilization treatment. On the other hand, as it is clear from the Reference Examples 3 and 4, in the case when syndiotactic polypropylene was not used, it was understood that it is a material where the water absorption was improved by the conducting of the hydrophilization treatment, however, the fiber strength after the hydrophilization treatment was significantly decreased. Also, as it is shown according to Table 5, even in the case where a blended type fiber is used where the amount of the syndiotactic polypropylene contained, is outside of the range defined according to the present invention, the same way, it was understood that the fiber strength after the hydrophilization treatment was significantly decreased.

[0047]

[Results from the present invention]

According to the above described, in the case of the present invention, it is an invention whereby it is possible to suggest a polyolefin type fiber with excellent hydrophilic properties, without sacrificing the inherent to the polyolefin mechanical strength, chemical resistant properties etc. And namely, this goal is achieved by conducting an oxidation treatment on the surface of a polypropylene fiber that is formed from syndiotactic polypropylene, a blended fiber that is formed from an olefin type polymer

and syndiotactic polypropylene, or a wick- shell type composite fiber, that has a structure obtained as the wick part is made from olefin type polymer and the shell part is made from syndiotactic polypropylene containing olefin type polymer. And by that it has become possible that polyolefin type fiber application sphere has been largely expanded to areas where in the past it has not been possible to use it because of the poor hydrophilic properties, or areas where it has not had a large market share.

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(54) 【発明の名称】 親水性に優れたポリオレフィン系繊維およびその製造方法

(57) 【要約】

【課題】 ポリオレフィンが本来有する力学的強度、耐薬品性等を損なうことなく、親水性に優れたポリオレフィン系繊維を得る。

【解決手段】 (1) シンジオタクチックポリプロピレンからなるポリプロピレン繊維、(2) シンジオタクチックポリプロピレンを30重量%以上含有するオレフィン系ポリマーからなるブレンド繊維、又は(3) 芯部がオレフィン系ポリマーで鞘部がシンジオタクチックポリプロピレンもしくはシンジオタクチックポリプロピレンを30重量%以上含有するオレフィン系ポリマーで構成された芯鞘型複合繊維の表面に、電子線照射法、 γ 線照射法、紫外線照射法、フォトン法、フレイム法、コロナ放電法、グロー放電法等の方法で酸化処理を行うことで酸素官能基を導入して親水性を付与する。

【特許請求の範囲】

【請求項1】 下記(1)～(3)の繊維の内から選択されたいずれか1種の繊維であって、該繊維表面に酸化処理により酸素官能基が導入されて親水性を有することを特徴とするポリオレフィン系繊維。

(1) シンジオタクチックポリプロピレンからなるポリプロピレン繊維。

(2) シンジオタクチックポリプロピレンを30重量%以上含有するオレフィン系ポリマーからなるブレンド繊維。

(3) 芯部がオレフィン系ポリマー、鞘部がシンジオタクチックポリプロピレンまたはシンジオタクチックポリプロピレンを30重量%以上含有するオレフィン系ポリマーで構成された芯鞘型複合繊維。

【請求項2】 請求項1に記載のポリオレフィン繊維を製造する方法であって、酸化処理により繊維表面に酸素官能基を導入するにあたり、電子線照射法、 γ 線照射法、紫外線照射法、フォトン法、フレイム法、コロナ放電法、およびグロー放電法から選ばれた少なくとも一つの方法を用いて酸化処理を行うことを特徴とするポリオレフィン系繊維の製造方法。

【請求項3】 酸化処理により繊維表面に酸素官能基を導入するにあたり、空気、酸素、窒素、CO、CO₂、He、Ar、硫黄酸化物および窒素酸化物の内から選ばれた少なくとも一種の気体を用いることを特徴とする請求項2記載のポリオレフィン系繊維の製造方法。

【請求項4】 アクリル酸、メタクリル酸、メタアリルスルホン酸、アリルスルホン酸、およびスチレンスルホン酸の内から選ばれた少なくとも一種の化合物を繊維表面にコーティングした後、該繊維表面に酸化処理により酸素官能基を導入することを特徴とする請求項2または請求項3記載のポリオレフィン系繊維の製造方法。

【請求項5】 請求項1に記載のポリオレフィン繊維を製造する方法であって、酸化処理により繊維表面に酸素官能基を導入するにあたり、繊維表面を、発煙硫酸、濃硫酸、およびクロルスルホン酸の内から選択された少なくとも一つの酸と接触させることを特徴とするポリオレフィン系繊維の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、ポリオレフィン系繊維に関するものであり、更に詳しくは、繊維の力学的強度を低下させることなく優れた親水性を付与してなるポリオレフィン系繊維に関するものである。

【0002】

【従来の技術】一般に、ポリエチレン、ポリプロピレン等のポリオレフィン、力学的特性に優れ、低比重であり、繊維加工性およびコストに優れ、さらには耐薬品性、特に高温での耐アルカリ性が非常に優れている。近年、これらの特徴を活かし、ポリオレフィン系繊維の産

業資材分野への進出、特に不織布分野への進出は著しいものがある。しかしながら、ポリオレフィン系繊維は接着性、親水性が大きく劣るため、ポリオレフィン系繊維の用途は限られているのが現状であり、これら欠点を改善することにより用途拡大が望まれている。

【0003】例えば、セメント補強用アスベスト代替繊維は、強度、高温下での耐アルカリ性、セメントとの親和性、水分散性等が要求されるが、ポリプロピレンはセメントとの親和性等に大きく劣るためその改良が望まれている。また、アルカリ電池用セパレータとしては、耐アルカリ性、親水性、耐酸化性等が要求される。さらに、汚過布等の湿式のフィルターも、同様に、耐薬品性、力学的強度の点からポリオレフィン、特にポリプロピレンが多く使用されているが、親水性の改善が望まれている。しかし、硫酸等による親水化処理法によりスルホン酸基を導入したものは、処理によりポリオレフィン繊維の劣化を伴い、力学的強度に劣る。また、プラズマ処理、電子線照射等を用いた気相法による親水化処理方法でも、同様に、ポリオレフィン繊維を劣化させる。このため、力学的特性と親水性のバランスに優れたポリオレフィン繊維の開発が望まれている。すなわち、上記のような方法で親水化処理すると、繊維の劣化が起こり、本来、ポリオレフィン系繊維が有している機械的特性が発現しなくなるため、親水化のレベルを下げるか、力学的強度を犠牲にせざるを得ないという欠点を有していた。さらには親水化レベルを向上させすぎると耐薬品性が低下する欠点も有していた。

【0004】

【発明が解決しようとする課題】本発明は、上記のような従来技術の有する問題点を解決し、力学的強度、耐薬品性等、本来、ポリオレフィンが有する性質を損なうことなく、親水性に優れたポリオレフィン系繊維を提供することにある。

【0005】

【課題を解決するための手段】本発明者らは上記課題について鋭意検討した結果、少なくとも繊維表面に、シンジオタクチックポリプロピレンを用いることにより、上記課題を解決しうることを見出し、本発明を完成するに至った。すなわち、本発明は、(1)シンジオタクチックポリプロピレンからなるポリプロピレン繊維、(2)シンジオタクチックポリプロピレンを30重量%以上含有するオレフィン系ポリマーからなるブレンド繊維、または、(3)芯部がオレフィン系ポリマー、鞘部がシンジオタクチックポリプロピレンまたはシンジオタクチックポリプロピレンを30重量%以上含有するオレフィン系ポリマーで構成された芯鞘型複合繊維、の内から選択されたいずれか1種の繊維であって、該繊維表面に酸化処理により酸素官能基が導入されて親水性を有することを特徴とするポリオレフィン系繊維である。

【0006】

【発明の実施の形態】本発明に用いるシンジオタクチックポリプロピレンとは、ベンダット分率が0.5以上のものを意味する。ここでベンダット分率とは、 ^{13}C -NMRで観測される約20ppmの強度（シンジオタクチックベンダットに相当）と全プロピレン単位のメチル基に帰属されるピーク強度との比のことである。従来、シンジオタクチックポリプロピレンを製造する際には、触媒としてバナジウム化合物を用いていたが、これではベンダット分率が0.5程度のものしか得ることができず、しかも大量に工業的に生産することも出来なかった。しかし、近年、非対称な配位子を有する遷移金属化合物とアルミノキサンからなる触媒によってベンダット分率が0.7を超えるようなタクティシティの高いポリプロピレンが得られるようになった。本発明で用いるシンジオタクチックポリプロピレンとしては、ベンダット分率が0.6以上のものが好ましく、より好ましくは0.7以上のものである。また、このシンジオタクチックポリプロピレンは、プロピレン単独重合体、またはプロピレンとエチレンおよび/または α -オレフィンとの共重合体からなる実質的にシンジオタクチックポリプロピレンであれば良い。

【0007】前記のようなシンジオタクチックポリプロピレンの製造法としては、例えば特開平3-179006号公報等に詳細に記載されている。重合触媒としては、互いに非対称な配位子を有する架橋型遷移金属化合物および助触媒を挙げることができるが、異なる構造を有する触媒であってもベンダット分率が0.6以上のポリプロピレンを製造できるものであれば利用でき、その重合法も特に限定するものではなく、不活性触媒を用いる溶媒重合法、または塊状重合法、気相重合法も利用できる。

【0008】次に、本発明におけるオレフィン系ポリマーとは、ポリエチレン、ポリプロピレン、ポリメチルペンテン等を意味し、またエチレン-プロピレン共重合体のように、これらのランダム共重合体、グラフト共重合体、ブロック共重合体であってもよい。本発明においては、これらオレフィン系ポリマーを単独で用いてもよく、またブレンドして用いてもよい。

【0009】シンジオタクチックポリプロピレンとオレフィン系ポリマーとのブレンド系繊維においては、シンジオタクチックポリプロピレンは30重量%以上、好ましくは40重量%以上使用するのが望ましい。30重量%未満では、親水性付与時に高分子鎖が劣化し難いというシンジオタクチックポリプロピレンの効果が現れないためである。

【0010】本発明のポリオレフィン系繊維を製造するための紡糸条件は特に限定されるものではなく、通常の方法で製造される。即ち、(1)のシンジオタクチックポリプロピレン繊維の場合には、紡糸温度として230

紡糸温度としては、鞘部はシンジオタクチックポリプロピレンを使用するため230~300℃、芯部は使用するポリオレフィン系ポリマーによるが、200~300℃が一般的である。同様に、(2)のブレンド系繊維の場合には、ブレンド比に応じて200~300℃に設定するのが一般的である。ブレンド方法も特に限定するものではなく、あらかじめ押出機でブレンドして得られたペレットを紡糸してもよく、また、各々のペレットまたはパウダーを所定量、重量フィーダーで供給しながら紡糸しても良い。また、本発明においては、力学的強度を向上させるため紡糸した繊維を3倍以上に延伸することが望ましく、熱水延伸が好ましい。

【0011】尚、本発明の繊維には、酸化防止剤、紫外線吸収剤等の安定剤、帯電防止剤、難燃剤、および染料、顔料等の着色剤を必要に応じて使用できることはいうまでもない。

【0012】次に、本発明における酸化処理とは、繊維表面に実質的に酸素官能基（ $-\text{COOH}$ 、 $-\text{OH}$ 、 $-\text{C}=\text{O}$ 、 $-\text{SO}_3$ 、 $-\text{NO}_3$ 基等）を導入することである。これらの官能基を繊維表面に導入することで、前記のようなオレフィン系繊維に親水性を付与することができる。

【0013】本発明において、繊維表面に酸素官能基を導入する酸化処理方法としては、電子線照射法、 γ 線照射法、紫外線照射法、フォトン法、フレイム法、およびコロナ放電法やグロー放電法などのプラズマ処理法が挙げられる。これら酸化処理方法は単独で使用しても良く、二種以上併用しても良い。これらの方法は、常温・常圧下で行ってもよいが、不活性ガスとして、 He 、 Ar 、反応性ガスとして、空気、酸素、窒素、 CO 、 CO_2 、硫黄酸化物（例えば SO_2 、 SO_3 等）、または窒素酸化物（例えば NO 、 NO_2 、 N_2O 等）の雰囲気中で行っても良い。これらの不活性ガスおよび反応性ガスは、電場をかけると種々の化学種（電子、イオン、ラジカル、励起分子等）を発生する。その結果、繊維を構成するポリマーと反応しやすくなり、繊維表面に酸素官能基が効果的に導入される効果をもたらす。

【0014】また、繊維表面に酸素官能基を導入するにあたり、親水性を発現するモノマーを、予め繊維表面にコーティングした後、酸化処理により酸素官能基を導入することもできる。この場合に繊維表面にコーティングする化合物としては、アクリル酸、メタクリル酸、メタアリルスルホン酸、アリルスルホン酸、スチレンスルホン酸などの親水性を発現するモノマーが挙げられる。これら化合物はコーティング後、電子線照射法、 γ 線照射法、プラズマ処理法等、上記酸化処理方法を用いて繊維表面に固着させる。これらの化合物は単独で用いても良く、二種以上併用しても良い。

【0015】本発明における、酸との接触による繊維表面の酸化処理方法は、酸としては、発煙硫酸、濃硫酸、

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およびクロルスルホン酸の内から選択されたものを用いる。これらは、単一で用いてもよく、また二種以上を混合して用いてもよい。繊維表面と酸との接触方法は特に限定しないが、これらの酸に該ポリオレフィン系繊維を直接浸漬する方法がよく用いられる。例えば濃硫酸を用いる場合は、50～120℃、5～60分の浸漬が一般的である。

【0016】

【作用】本発明に従えば、シンジオタクチックポリプロピレンを用いることで、ポリオレフィン系繊維の劣化を
10 引き起こすことなく、その表面に親水化処理を施すことができる。その結果、ポリオレフィン系繊維が本来有す*

表1 樹脂特性

	MFR ^(*) (g/10分)	その他
ポリプロピレン(1)	30	—
シンジオタクチックポリプロピレン	25	ペンダット分率 0.78
ポリエチレン(1)	23	—

(*) MFR:メルトフロー値(下記の測定法による。)

①ポリプロピレンの場合: JIS K 6758
②ポリエチレンの場合: JIS K 6760

【0020】(シンジオタクチックポリプロピレンの重合)表1に示したシンジオタクチックポリプロピレンは、以下のようにして重合したものである。まず、J. Am. Chem. Soc. 1987年、109号、p6544の記載に従い、イソプロピルシクロペンタジエニル-1-フルオレンをリチウム塩に転化し、四塩化ジルコニウムと反応させることで、イソプロピル(シクロペンタジエニル-1-フルオレニル)ジルコニウムジクロ
30 リドを合成した。次に、0.33mmolのトリエチルアルミニウムを2mlのトルエンに溶解させて反応器に加え、反応器温度を70℃に設定した。そして1500mlのプロピレンを反応器に加え、10分間攪拌した。45mgのトリス(ペンタフルオロフェニル)ボロンを20mlのトルエンに溶解、同様に35mgのイソプロピル(シクロペンタジエニル-1-フルオレニル)ジル
40 コニウムクロリドを25mlのトルエンに溶解後、2種の前記トルエン溶液を5分間一緒に混合した。この触媒混合物を50mlのステンレス鋼ボンベに加えた後、該
50 ボンベを通じて上記反応器中に200mlのプロピレンを加えた。反応器の内容物を約30分間攪拌し反応させた。未反応のプロピレンを反応器から排気後、反応生成物をアセトンで洗浄し、真空下で乾燥した。

【0021】(シンジオタクチックポリプロピレンのタクティシティー測定) ¹³C-NMRで観測される約20ppmの強度(rrrr)と全プロピレン単位のメチル基に帰属されるピーク強度(mm、mr、rr)との比を測定し、下式によりシンジオタクチックペンダット分率を算出した。

* 力学特性、耐薬品性を損なうことなく、親水性と力学特性、さらには耐薬品性のバランスに優れたポリオレフィン系繊維を提供することができる。

【0017】

【実施例】以下、実施例にて本発明を具体的に説明する。尚、本発明は以下の実施例に限定されるものではない。

【0018】(樹脂特性)表1に以下の実施例、比較例に使用した樹脂の特性を示す。

【0019】

【表1】

※【0022】シンジオタクチックペンダット分率(%)
= rrrr / (mm + mr + rr) × 100

【0023】(実施例1)表2に示す条件で、シンジオタクチックポリプロピレンを溶融紡糸したのち熱延伸し、繊維3d(デニール、以下同じ。)のフィラメントおよび繊維長51mmのステープルを得た。次にこのステープルを用い、ローラーカード機を通してウェブを作成し、スパンレース機により目付40g/m²の不織布シートを得た。次に、この不織布シートおよび前記フィラメントを反応器に入れ、常温・常圧下で200KVの印加電圧を用いてコロナ放電処理することで、繊維表面の親水化処理を行った。

【0024】(実施例2)表2に示す条件で、ポリプロピレン(1)を60重量%とシンジオタクチックポリプロピレンを40重量%とをブレンドして溶融紡糸したのち熱延伸し、繊維3dのフィラメントおよび繊維長51mmのステープルを得た。次に実施例1と同様にして目付40g/m²の不織布シートを得た。次に、この不織布シートおよび前記フィラメントを実施例1と同じ条件でコロナ放電処理し、繊維表面の親水化処理を行った。

【0025】(実施例3)表2に示す条件で、ポリエチレン(1)を30重量%とシンジオタクチックポリプロピレンを70重量%とをブレンドして溶融紡糸したのち熱延伸し、繊維3dのフィラメントおよび繊維長51mmのステープルを得た。次に実施例1と同様にして目付40g/m²の不織布シートを得た。次に、この不織布シートおよび前記フィラメントを実施例1と同じ条件でコロナ放電処理し、繊維表面の親水化処理を行った。

【0026】(実施例4)実施例2で得られたと同じフィラメントおよび不織布シートをアクリル酸に浸漬後、反応器に入れ、窒素雰囲気下で電子線を4Mrad照射させることで、繊維表面の親水化処理を行った。

【0027】(実施例5)実施例2で得られたと同じフィラメントおよび不織布シートをアクリル酸に浸漬後、反応器に入れ、波長が200nm以上の紫外線を照射させることで、繊維表面に親水化処理を行った。

【0028】(実施例6)実施例2で得られたと同じフィラメントおよび不織布シートを反応器に入れ、He7*10

表2 紡糸条件

	重合比 (%)	紡糸温度 (℃)	延伸倍率 (倍)	延伸温度 (℃)
実施例1	100 (s-PPのみ)	260	3.5	80
実施例2	ブレンド (s-PP/PP1=40/60)	250	3.5	70
実施例3	ブレンド (s-PP/PP1=70/30)	250	3.5	70
実施例4	ブレンド (s-PP/PP1=40/60)	250	3.5	70
実施例5	ブレンド (s-PP/PP1=40/60)	250	3.5	70
実施例6	ブレンド (s-PP/PP1=40/60)	250	3.5	70
実施例7	100 (s-PPのみ)	260	3.5	80

PP1 : ポリプロピレン(1)

s-PP : シンジオタクチックポリプロピレン

PE : ポリエチレン(1)

【0031】(実施例8)表3に示す条件で、芯部にポリプロピレン(1)、鞘部にシンジオタクチックポリプロピレンを配する芯鞘型複合繊維を熔融紡糸したのち熱延伸し、繊度3dのフィラメントおよび繊維長51mmのステープルを得た。次にこのステープルを用い、ローラーカード機を通してウェブを作成し、スパンレース機により目付40g/m²の不織布シートを得た。次に、この不織布シートおよび前記フィラメントを反応器に入れ、常温・常圧下で200KVの印加電圧を用いてコロナ放電処理することで、繊維表面に親水化処理を行った。

【0032】(実施例9)表3に示す条件で、芯部にポリプロピレン(1)、鞘部にシンジオタクチックポリプロピレンとポリプロピレン(1)とのブレンドポリマーを配する芯鞘型複合繊維を熔融紡糸したのち熱延伸し、繊度3dのフィラメントおよび繊維長51mmのステープルを得た。次に、このステープルを用い、ローラーカード機を通してウェブを作成し、スパンレース機により目付※

*0%、空気30%の雰囲気中、常温・常圧下で高周波電圧5KHzを印加しグロー放電させることで、繊維表面に親水化処理を行った。

【0029】(実施例7)実施例1で得られたと同じフィラメントおよび不織布シートを、80℃に加熱した98%濃硫酸に20分間浸漬後、中和、水洗、乾燥して、繊維表面に親水化処理を行った。

【0030】

【表2】

30※40g/m²の不織布シートを得た。次に、この不織布シートおよび前記フィラメントを反応器に入れ、常温・常圧下で200KVの印加電圧を用いてコロナ放電処理することで、繊維表面に親水化処理を行った。

【0033】(実施例10)実施例8で得られたと同じ不織布シートおよびフィラメントを、スチレンスルホン酸に浸漬後、反応器に入れ、窒素雰囲気下で電子線を4Mrad照射させることで、繊維表面に親水化処理を行った。

【0034】(実施例11)実施例8で得られたと同じフィラメントおよび不織布シートを反応器に入れ、Ar90%、窒素、水素、酸素、CO₂の混合ガス10%の雰囲気中、常温・常圧下で高周波電圧5KHzを印加しグロー放電させることで、繊維表面に親水化処理を行った。

【0035】

【表3】

表3 紡糸条件

	重量比 (%)		紡糸温度 (°C)		延伸倍率 (倍)	延伸温度 (°C)
	芯部	鞘部	芯部	鞘部		
実施例8	PP1=70	s-PP=30	250	260	3.5	70
実施例9	PP1=60	s-PP/PP1=20/20	250	260	3.5	70
実施例10	PP1=70	s-PP=30	250	260	3.5	70
実施例11	PP1=70	s-PP=30	250	260	3.5	70

PP1 : ポリプロピレン(1)

s-PP : シンジオタクチックポリプロピレン

【0036】(比較例1)表1に示すポリプロピレン(1)のみを用いて表4の条件で熔融紡糸したのち熱延伸し、織度3dのフィラメントおよび繊維長51mmのステープルを得た。次に、このステープル繊維を用い、実施例1と同様な方法で目付40g/m²の不織布シートを得た。

【0037】(比較例2)実施例1で得られたシンジオタクチックプロピレンのフィラメントの強度、および不織布シートの吸水度を測定した。

【0038】(比較例3)比較例1にて得られたと同じフィラメントおよび不織布シートを、実施例1と同じ条件でコロナ放電処理し、繊維表面に親水化処理を行った。

【0039】(比較例4)比較例1にて得られたと同じフィラメントおよび不織布シートを、実施例4と同じ条*

*件でアクリル酸に浸漬後、反応器に入れ、窒素雰囲気下で電子線を4Mrad照射させることで、繊維表面に親水化処理を行った。

【0040】(比較例5)表4に示す条件で、ポリプロピレン(1)を90重量%とシンジオタクチックポリプロピレンを10重量%とをブレンドして熔融紡糸したのち熱延伸し、織度3dのフィラメントおよび繊維長51mmのステープルを得た。次に、このステープル繊維を用い、実施例1と同様にして目付40g/m²の不織布シートを得た。次に、この不織布シートおよびフィラメントを実施例1と同じ条件でコロナ放電処理し、繊維表面に親水化処理を行った。

【0041】

【表4】

表4 紡糸条件

	重量比 (%)	紡糸温度 (°C)	延伸倍率 (倍)	延伸温度 (°C)
比較例1	100 (PP1のみ)	250	3.5	70
比較例2	100 (s-PPのみ)	260	3.5	80
比較例3	100 (PP1のみ)	250	3.5	70
比較例4	100 (PP1のみ)	250	3.5	70
比較例5	ブレンド s-PP/PP1=10/90	250	3.5	70

PP1 : ポリプロピレン(1)

s-PP : シンジオタクチックポリプロピレン

【0042】以上の実施例1~11および比較例1~5で得られたフィラメントの強度、および不織布シートの吸水度を測定した結果を表5に示す。尚、物性評価方法は以下に示す通りである。

【0043】〔吸水度〕得られた不織布シートを試料巾25mm、長さ300mmに調製し、イオン交換水にシート的一端を垂直に浸漬(浸漬高さ20mm)し、10分後の吸液高さ(mm)を求め、これを吸水度とした。

【0044】〔繊維の引張強度〕得られたフィラメント(親水化処理前および処理後)を、JIS L 101※50

※3の方法で測定した。

【0045】

【表5】

表5 物性表

	強度 (g/d)		吸水度 (mm)
	処理前	処理後	
実施例1	7.2	6.8	152
実施例2	5.9	5.1	147
実施例3	4.8	4.2	137
実施例4	5.9	5.3	150
実施例5	5.9	5.1	144
実施例6	5.9	5.4	145
実施例7	7.2	6.1	148
実施例8	6.3	5.9	153
実施例9	6.6	6.0	146
実施例10	6.3	5.7	132
実施例11	6.3	5.8	170
比較例1	6.6	—	19
比較例2	7.2	—	21
比較例3	6.6	3.2	148
比較例4	6.6	3.0	152
比較例5	6.3	3.8	150

処理前：親水化処理前
処理後：親水化処理後

【0046】比較例1、2より、通常のポリプロピレン

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およびシンジオタクチックポリプロピレンのいずれを用いても、親水化処理を行わないと、吸水度が非常に劣ることが判る。また、実施例1～11に示すように、いずれの親水化処理方法を用いても吸水度が非常に向上し、且つ親水化処理前後での繊維強度がほとんど変化しないことが判る。一方、比較例3、4から明らかなように、シンジオタクチックポリプロピレンを用いない場合は、親水化処理により吸水度は改善されるものの、親水化処理後の繊維強度の低下が著しいことが分かる。また、比較例5に示すように、ブレンド系繊維でシンジオタクチックポリプロピレンの量が本発明の範囲外である場合も、同様に、親水化処理後の繊維強度低下が著しいことが分かる。

【0047】

【発明の効果】以上のように、本発明によれば、力学的強度、耐薬品性等の、ポリオレフィンが本来有する性質を損なうことなく親水性に優れたポリオレフィン系繊維を提供することができる。すなわち、シンジオタクチックポリプロピレン繊維、またはシンジオタクチックポリプロピレンとオレフィン系ポリマーとのブレンド系繊維、または芯部がポリオレフィン系ポリマーで鞘部がシンジオタクチックポリプロピレン含有オレフィン系ポリマーから構成される芯鞘型複合繊維の繊維表面を酸化処理することにより、上記の目的が達成される。これにより、従来、親水性に劣るため使用できなかった、あるいは市場が拡大していない分野へのポリオレフィン系繊維の応用が可能となった。

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